Journal of Scientific Research & Reports

27(4): 27-52, 2021; Article no.JSRR.66589
ISSN: 2320-0227

Adsorption of Crude Oil Spill from Aqueous Solution using Agro-Wastes as Adsorbents

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Authors' contributions

This work was carried out in collaboration among all authors. Author AOO designed the study, wrote the protocol and wrote the first draft of the manuscript. Author AAO managed the analyses of the study and managed the literature searches. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JSRR/2021/v27i430376
Editor(s):
(1) Dr. Lesław Juszczak, Agricultural University of Kraków, Poland.
Reviewers:
(1) Mozammel H Mazumder, University of Notre Dame, USA.
(2) Munshi Md. Shafwat Yazdan, Idaho State University, USA.
Complete Peer review History: http://www.sdiarticle4.com/review-history/66589

Original Research Article

Received 17 February 2021
Accepted 23 March 2021
Published 29 May 2021

ABSTRACT

Ever increasing and growing awareness of oil-spillage to water environment has led to the search for cost-effective unconventional remediating techniques. This study was carried out using agro-wastes (Rice Husks, Banana Peels and Groundnut Husks) adsorbents. They were activated with H_3PO_4 for crude oil spill removal from aqueous solution; results were analysed using atomic absorption spectroscopy. The raw agro-wastes and their activated forms were characterized by SEM. The sorption study for maximum adsorption capacity were carried out at different adsorbent concentrations, adsorbent dosage, contact time, pH and rotational speed. The experimental results were analysed using Langmuir, Freundlich, Temkin, Dubinin-Radushkevich isotherm models. The maximum average adsorption capacity (q_e) for raw and activated carbon adsorbents were observed in rice husks with 0.2750 and 0.3698 mg/g respectively. The Langmuir isotherm was found to well represent the measured sorption data for the raw and activated banana peel while the remaining raw and activated adsorbents followed the Temkin isotherm. The batch adsorption data on the effect of contact time were fitted into the pseudo-first-order and pseudo-second order models. The banana peel data and its activated form were best described by the pseudo-second-order model indicating chemisorption process while the remaining adsorbents followed the pseudo-first-order model indicating physisorption process. The average removal efficiency of oil by the various

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adsorbents used increase in the order: (Raw: Banana Peels (50.4 %) < Groundnut Husks (56.8 %) < Rice Husks (74.4 %); Activated Carbon: Banana Peels (61.4 %) < Groundnut Husks (65.6 %) < Rice Husks (82.8 %)). Results of this study (high values of R^2 and least values AARE and RMSE) revealed and confirmed that activated carbon adsorbents have better adsorption capacity than the raw forms to clean-up oil spills in aqueous solution.

Keywords: Activated carbon; adsorbent; adsorption capacity; isotherm model; sorption of crude oil.

ABBREVIATIONS

A (L/g)	-	*the Temkin isotherm constant adsorption capacity and intensity, respectively.*
b	-	*Langmuir constants related to the energy of adsorption*
B (J/mol)	-	*the Temkin constant related to heat of sorption*
C_e *(mg/L)*	-	*the equilibrium concentration of the adsorbate in solution.*
k_1 *(1/min)*	-	*the rate constant of the pseudo-first-order model.*
k_f *and n*	-	*constants incorporating all factors affecting the adsorption such as*
q_e *(mg/g)*	-	*the amount of adsorbate adsorbed by the sorbent at equilibrium time*
Q_o	-	*Langmuir constants related to the adsorption capacity*
q_t *(mg/g)*	-	*the amount of adsorbate adsorbed by the sorbent at time t*
R	-	*the gas constant (8.314 J/mol K)*
T (°K)	-	*the temperature*

1. INTRODUCTION

Water is well known as an important source of life worldwide, but is increasingly being polluted by oil spillage leading to poor surface and ground water quality; these remains a serious concern in oil producing regions of the world. The author [1] reported that authorities on yearly basis contend with hazards of crude oil spillage on both aquatic and terrestrial ecosystems. Reliable access to clean and affordable water was considered as one of the main human goals in the twenty-first century [2-3]. Water (environmental) pollution by petroleum hydrocarbons and its derivatives have been considered [4-5] as important pollutants and of serious concern to the developed and developing countries.

Oil spills in the aquatic environment are major environmental hazards, many aquatic animals have been harmfully affected and it was reported an estimated 2 billion dollars have been spent on cleaning up [6]. Water contaminated by oil can be disastrous depending upon the nature of the petroleum fraction, the way and time of exposure to it. Organic contaminants are not the only pollutants associated with oil spills but inorganic contaminants e.g. Cobalt (Co), Nickel (Ni), Copper (Cu), Lead (Pb), Iron (Fe), Vanadium (V) etc. also get introduced into the oil, which contaminates the water and may become pollutants once their concentration exceeds the tolerable limit set by the international standards [7]. These inorganic toxic elements are not biodegrading, and so can progressively accumulate in the ecosystem until an intolerable level is reached leading to several public health issues [7].

To avert these dangers, there is an urgent need to treat oil spill contaminated water and other related waste water to bring about a reduction in the concentrations of both organic pollutants and the potentially toxic elements to acceptable levels as approved by national and international guidelines before their final discharge into the environment.

Literatures are replete in oil spillage clean-up [7-10], the different techniques for oil pollution clean-up are as shown in Fig. 1. The sorption process is one of the efficient, easiest, and cost effective methods for decontamination of oil pollutions [11-13]. Among the used sorbents, the biosorbents are biodegradable, non-toxic, and low cost [11,14,15,16] Various biosorbents including cattail fibers [10], rice husk [17], cotton fibers [6], Azollafiliculoides biomass [18], straw biomass waste [19], and lignocellulosic biomass of pineapple leaves [13] were used for the removal of oil from aqueous solutions. With increasing environmental awareness and legal constraints imposed on oil spillage, the need to develop cost-effective alternative technologies for removal of potentially toxic elements and soluble petroleum fractions from water contaminated by oil is essential. Considerable attention has been devoted to the development of unconventional materials such as agricultural by-products for remediating oil spillage. This is due to the fact that they are readily available, affordable; eco-friendly and can have high uptake capacity due to the presence of functional groups which can bind metals [5].

1.1 Rice Husk

It is well known that rice is the most important staple food crop consumed worldwide. In 2004, Erenstein et al. [22] reported a 14% annual increase in the demand for rice in Nigeria; rice cultivation is widespread within the country under five production systems (or ecologies) classified as rain-fed upland, rain-fed lowland, irrigated lowland, deepwater, and mangrove swamp accounting for 30%, 47%, 17%, 5%, and 1% of the total rice areas, respectively. Nigeria has been on the path of boosting its rice production which will invariably lead to increased generation of rice husk (as solid waste) in the environment [23]. Not only rice husk, their charcoal obtained from combustion step is also versatile. Both rice husk and rice husk charcoal have major components namely, carbon and silica. They have been found to be suitable materials owing to their high carbon and silica and low ash contents. Consequently, they are determined to be the precursors used for the production of activated carbon that is commonly used as adsorbents. Activated carbons have exceptional adsorption properties because of their high surface area, large adsorption capacity and fast adsorption kinetics. Thus, a possible solution for rice husk is converting it into value-added activated carbon used as adsorbents. Therefore, one of the objective of this work is to highlight the applicability of rice husk activated carbon in the adsorption of crude oil components from polluted waters using adsorption mechanism.

1.2 Banana Peel

As one of the most consumed fruits in the world, banana is a very common fruit. Preliminary investigations showed that several tons of banana peels are produced daily in market places and household garbage, creating an environmental nuisance and disposal problem [24]. Various chemical groups exist on the banana peel surface, including carboxyl, hydroxyl and amide groups [25], which have been extensively proven to play a critical role in the adsorption processes (e.g. enhancing adsorption capacity and shortening stable time). Bananas are rich in antioxidant vitamins (vitamins C, A, and E), calcium (Ca), magnesium (Mg), and potassium (K). Bananas are considered nutritive with high content of vitamins A and C but poor in vitamins B. Bananas are used fresh or processed into many products such as chips, powder, jams, juice, bar, biscuits, wine etc. [26]. At present, these peels are not being used for any other purposes and are mostly dumped as solid waste at large expense. It is thus significant and even essential to find applications for these peels as they can contribute to real environmental problems [27].

1.3 Groundnut Husk

Groundnut husk is a carbonaceous, fibrous solid waste which encounters disposal problem and is generally used for its fuel value. The cultivated peanut or groundnut (Arachishypogaea L.) originated in South America (Bolivia and adjoining countries) and is now grown throughout the tropical and warm temperate regions of the world. This crop was grown widely by native people of the New World at the time of European expansion in the sixteenth century and was subsequently taken to Europe, Africa, Asia, and the Pacific Islands. In this work, groundnut shell, a locally sourced agricultural waste is used as adsorbent for the batch removal of crude oil from water. This adsorbent is not only economical and biodegradable but can also be used for composting. The major traditional mainstay of the Nigerian nation is agriculture, while groundnut is one of her major produce. The estimated annual production of groundnut for 2002 and 2003 are 2,390,000 and 2,690,000 metric tons respectively. The groundnut husks are littered around the environment, thereby constituting nuisance, whereas it could be used as biosorbent because it is largely composed of cellulose and lignin. The objective of this research is to study and evaluate the adsorption of crude oil from polluted water using meshed groundnut shell as one of the adsorbent.

1.4 Adsorbents in the Petroleum Spills Clean-up

Sorbents used in the removal of oil spills have been classified into three main groups, depending on the source of origin: Inorganic mineral sorbents; Natural organic sorbents and Synthetic organic sorbents i.e. synthetic polymers [10,15].

Mineral adsorbents represent large group; they are commonly used as they have number of advantages such as non-flammability, chemical inertness, relatively low cost and easy availability. They are also known as sinking sorbents, and they are highly dense, fine-grained materials natural or processed used to sink floating oil. They can be considered as a group of universal adsorbents; most mineral adsorbents are raw materials of natural origin which are used in a powder or granular form. Their primary disadvantage is a risk of dust formation during application in open spaces, and respiratory protective equipment and eye protection are therefore required when using certain powder sorbents. They are not generally preferred for the removal of oil spills from water surfaces because of their low buoyancy and low oil absorbability when compared to polymers or natural organic sorbents [9].

Natural organic adsorbents used in chemical rescue include peat, needle-cover, moss, dry leaves, straw, sawdust, bark and wood waste, cellulose from paper and cotton products, linen materials, cotton and hemp. The literature also describes other sorbents of natural origin from agricultural and processing wastes, such as rice husk, various types of plant shells and plant waste, kapok and many others [9,28]. Natural organic adsorbents are considered to be effective, inexpensive (although this is not universally true), easy available and environmentally friendly. They are biodegradable and flammable, and thus are easy to utilize. However, their low bulk density and lightness may cause an impediment in open spaces, and their poor buoyancy limits their use in an aqueous environment. It is impossible to use them in the case of fire. Of the natural organic adsorbents, the most efficient are those subjected to special (thermal) treatment [15,29].

The group of synthetic polymers includes polypropylene, polyethylene, polyacrylate, polystyrene, and polyurethane, which are used to manufacture special sleeves, mats, cloths, or cushions for the sorption of hazardous liquids. Polymer adsorbents exhibit hydrophobic properties, low bulk density, and large sorption capacity with respect to petroleum derivatives [30,31]. Due to their buoyancy and hydrophobicity they are mainly used in aqueous media and very rarely for the removal of oil spills from rigid pavements, since they are often too light and easily blown by the wind. Further disadvantages of these materials are the possibility of returning the absorbed liquid under external forces, non-biodegradability and flame retardant properties. Their utilization also involves the problem of emission of toxic compounds during combustion. Although methods which allow the recovery of the synthetic polymer sorbents after oil sorption, such as centrifugation and pressing, are known, these are very limited due to the destruction of the structure of the sorbent, oxidation or strong contamination.

1.5 Sorption Isothermal Studies and kinetics Model

Essential data such as mechanism of adsorption, adsorption process favorability and adsorbate-adsorbent affinity [32] may be obtained from the following sorption isothermal studies: Langmuir [31,33]; Freundlich [32,34]; Tempkin [32,35]; Dubinin and Radushkevich [5,36,37,38] were used to evaluate the rate of oil sorption by the adsorbents. The experimental data were described by the Lagergren pseudo-first order [39,40] and pseudo-second order [40,41] kinetic models. The pseudo-first order kinetic model mathematical expression is given as:

$$\frac{dq}{dt} = k_1.(q_{e1} - q_t) \tag{1}$$

By integrating the boundary conditions of q_t=0 at t=0, the pseudo-first-order model gives:

$$\ln(q_{e1} - q_t) = \ln(q_{e1}) - k_1 t \tag{2}$$

Where ln (q_{e1}) is the intercept of ln (q_e − q_t) plotted versus t in the straight line form. The pseudo-second-order kinetic model is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

Where k_2 (g/mg min) is the rate constant determined from the slope of plot of t/qt versus t [42].

1.5.1 Sorption Isotherms

According to Foo and Hameed [43], sorption isotherms are important for optimizing the sorption process and describing the sorption mechanism, they openly presented cutting-edge analysis of adsorption isotherm models. The data obtained from the sorption experiments were evaluated by the Langmuir, Freundlich, Temkim and Dubinin-Radshkevich adsorption isotherm models.

1.5.1.1 The langmuir isotherm

The mathematical form of Langmuir model which describes a monolayer and homogeneous sorption process on the surface of adsorbent and the sorption energies to be equivalent for each sorption site was expressed by the researchers [5, 9,32,33] and given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \qquad (4)$$

When C_e/q_e is plotted against Ce gives a straight line with gradient $1/Q_o$ and intercept of $1/Q_{ob}$.

1.5.1.2 The freundlich isotherm

Non-ideal systems can sometimes be fitted to an empirical adsorption isotherm developed by the German physical chemist Herbert Max Finlay Freundlich [5,34] known as the Freundlich equation is given as:

$$\log q_e = \log k_f + \frac{1}{n \log C_e} \qquad (5)$$

Values of k_f and n may be calculated by plotting log (q_e) versus log (C_e), the slope is equal to 1/n and the intercept is equal to log (k_f). The Freundlich model is based on an exponential distribution of sorption sites and energies. It is an empirical model not limited to monolayer coverage alone but also describe multilayer (i.e. heterogeneous systems) adsorption [32].

1.5.1.3 Temkin adsorption isotherm

The Temkin model (equation 6) was tested for equilibrium description at room temperature. Plotting q_e versus ln C_e enables the determination of the constants A and B [35-44].

$$q_e = B \ln(A + C_e)$$
$$where : B = \frac{RT}{b} \qquad (6)$$

In their work, Inyinbor et al. [32] stated that the Temkin isotherm assumes linear and not logarithm decrease of heat of adsorption; they also indicated that the isotherm assumes uniform distribution of bounding energy up to some maximum bonding energy.

1.5.1.4 Dubinin-radushkevich isotherm

This isotherm model is a more general model in which assumption is not based on homogenous surface or constant adsorption potential, it was chosen to estimate the characteristics biomass porosity and the apparent adsorption energy which provides information if adsorption process is either physical or chemical in nature [32]. The model is expressed mathematically as:

$$q_e = q_D \exp^{-\left(2B_D RT \ln\left(1+\frac{1}{C_e}\right)\right)} \qquad (7)$$

Where B_D is related to the free energy of sorption per mole of the adsorbate as it migrates to the surface of the biomass from infinite distance in the solution and q_D is the Dubinin-Radushkevich isotherm constant related to the degree of adsorbate sorption by the sorbent surface [36,45]. The linear form of equation is given as:

$$\ln q_e = \ln q_D - 2B_D RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (8)$$

In 2013, Kudaibergenov et al. [46] thermally treated adsorbents using rice husks as efficient absorber for heavy crude oil while Razavi et al. [17] in their studies stated that raw rice husk was used as a low cost adsorbent to remove three oil compounds with varying viscosities (crude oil, engine oil and spent engine oil) from an aqueous environment. Their findings disclosed that adsorption of crude and spent oils on rice husk followed the Freundlich isotherm model, while the adsorption of engine oil was fitted by the Langmuir model.

In 2014, Mohammad et al [47] observed the effects of bed depth of rice husk activated carbon and flow rate of the waste water on the sorption of phenol from the waste water. The adsorption capacity of 28mg/g at breakthrough point of 0.5, flow rate of 4.5ml/min and bed depth of 7.5cm was attained. While in 2017, Gabriela et al. [48] used activated carbon from rice husk which was chemically treated by K_2CO_3, as sorbent phase for trace analysis of carbazole in commercial diesel; their result demonstrated an acceptable adsorption capacity.

Somaia et al. [49] investigated the removal of cadmium (II) from aqueous solution by using low cost, natural and eco-friendly adsorbent of banana peels activated carbon through batch experiments. They discovered that removal of Cadmium ions from wastewater was largely influenced by pH of the synthetic wastewater and the amount of biosorbent dose. Their equilibrium adsorption data fitted to Langmuir adsorption isotherm model. In 2017, G. Alaa El-Din et al. [50] examined the oil sorption capacity of crude and gas oils using banana peel as a substitutional material from local fruit wastes. The research detected that the capacity of banana peel as sorbent to clean up crude oil from produced water toward different factors was associated with surface characteristics, oil type, oil film thickness, sorption time, temperature, as-well-as salinity of crude oil.

Darlington and Uchenna in their study [51] used low cost biodegradable groundnut shell as adsorbent. The groundnut husk was treated and meshed to adsorb crude oil from water at various experimental conditions and the effects of sorbent dosage, particle size, contact time and temperature on the adsorption of crude oil was determined. Their findings revealed that crude oil removal from water by adsorption using groundnut shell is possible. Medjor et al. [52] looked at the effectiveness of activated carbon from groundnut husk for the adsorption of phenol. Optimum conditions of carbon dosage, pH, contact time and influence of concentration of phenol on carbon were investigated. Several analyses of isotherm data were tested by fitting them into different isotherm (Temkin, Langmuir, Dubinin-Kaganer-Rushkevich and Freundlich) models. The adsorption of phenol by the activated carbon was best described by Freundlich model with regression coefficient of 0.9501.

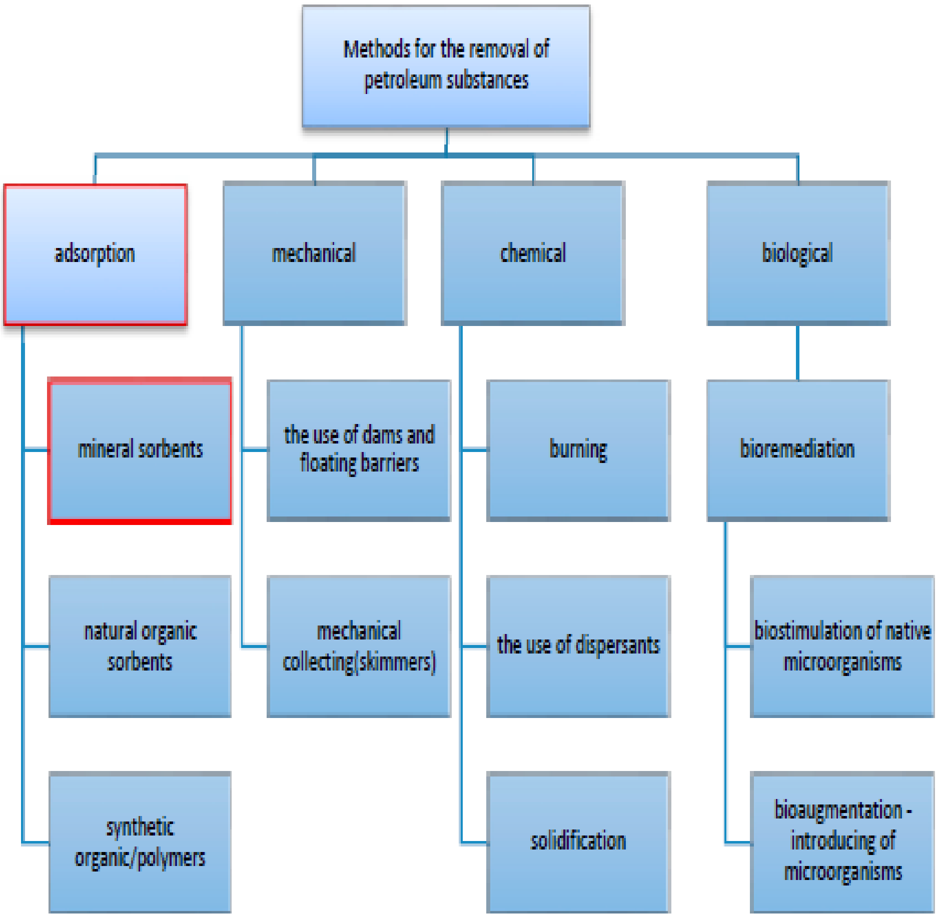


Fig. 1. Methods used for the removal of petroleum substance [20, 21]

A Review of Algae-Based Produced Water Treatment for Biomass and Biofuel Production:

In this study we used agricultural wastes of rice husk, groundnut husk and banana peel as adsorbents to remove and clean up crude oil spills from water. The effectiveness of agricultural waste materials as adsorbent were studied both in their natural states and chemical modification form. Their kinetic and thermodynamic properties were determined. We employed Langmuir, Freundlich, Temkin and Dubinin Radushkrvich isotherm models to evaluate the sorption capacity of the adsorbents as well as to determine the kinetics and optimum parameters under which adsorption of crude oil with the eight adsorbents are most effective. Also, scanning electron microscope (SEM) was used to analyse the quantity of oil adsorbed by each sorbent by characterizing the sorbents before and after the experiment.

2. MATERIALS AND METHODS

2.1 Materials

The following materials and apparatus were utilized for the experimental work:

Beakers, conical flasks, measuring cylinder, electric muffle furnace, electronic mass balance, filter paper, Jayant 8-inch Diameter Mesh (BSS 300) Test Sieves, oven, pH meter, spatula, orbital shaker, Perkin Elmer Lambda25 UV-VIS spectrophotometer, de-ionized water, crude oil, groundnut husk, banana peels, rice husk, phosphoric acid.

2.2 Preparation of Simulated Crude-oil Spill

The crude oil sample used for this research work was obtained from the Nigeria Petroleum Development Company (NPDC), River State, Nigeria. A typical small oil spill of 0.025 g/L initial concentration was simulated by pouring 25 g of crude oil into 1,000 ml of distilled water in a beaker.

2.3 Agro-Wastes

Agro-wastes are viable options for remediation of polluted water [40] because of their distinctive chemical composition, availability, renewability, low-cost and eco-friendly [10] attributes; hence there is increased attention on utilization of agricultural wastes in adsorption processes. These agricultural waste materials from published studies include: rice bran and rice husk [53,54], wheat bran, wheat husk, saw dust of various plants, bark of the trees, groundnut shells, coconut shells, black gram husk, hazelnut shells, walnut shells, cotton seed hulls [55], waste tea leaves, cassia fistula leaves, maize corn cob, jatropha, de-oiled cakes, sugarcane bagasse, banana, orange peels, soybean hulls, grapes stalks, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans, and cotton stalks, etc. [10].

More increasing demands for food production in Nigeria have led to additional generation of agricultural wastes which increase additional challenges in solid waste disposal. For example, in an attempt to become self-sufficient in rice production, Nigeria has been on the path of boosting its rice production which will invariably lead to increased generation of rice husk (as solid waste) in the environment [23]. Rice husk, banana peels and groundnut husk are the agricultural wastes used in this research work.

2.3.1 Preparation of rice husk adsorbent

The rice husk sample was collected from a local rice miller in Ilorin, Kwara state and was grounded and sieved into different particle sizes for the adsorption experiments. Rice husk was soaked with distilled water for 1 day and then dried using furnace at 110 ºC for 4 hours, after drying, it was stored in tightly closed bottle.

The activated carbon was prepared through chemical activation. 100 g of the rice husk powder with 200 ml of concentrated H_3PO_4 (1:2 weight ratios) for 3 hours in an air condenser system. After cooling, the final products were filtrated and washed several times with sodium bicarbonate solution and distilled water till neutral pH. After that, the resultant precipitate was dried at 110°C for 24 hours, and subsequently was weighed to determine the yield of the product. Finally, it was stored in tightly closed bottle.

2.3.2 Preparation of banana peels adsorbent

Fresh banana peels were collected from local stores in Bodija, Ibadan, Oyo state. The collected peels were first washed by distilled water, and then dried for 7 days in oven at 110 °C for 24 hours. After drying, the peels were crushed and sieved to 125 mm sieve and was stored in tightly closed bottle. The activated carbon was prepared through chemical activation. 40 g of the fruit peel powder with 120 ml of concentrated H_3PO_4 (1:3 weight ratios) for 6 hours in an air condenser system. After cooling, the final products were filtrated and washed several times with sodium bicarbonate solution and distilled water till neutral pH ~ 7. After that, the resultant precipitate was dried at 110 °C for 24 hours, and subsequently was weighed to determine the yield of the product. Finally, it was stored in tightly closed bottle [50].

2.3.3 Preparation of groundnut husk adsorbent

The groundnut husks adsorbent was sourced from local groundnut oil processing plant. It was washed with de-ionized water to remove any impurity and dried in an oven, to remove any moisture/water in it, and stabilize its weight. After which, it was meshed, sieved and stored in tightly closed bottle. 200 g of the meshed groundnut husks were taken and was subsequently treated with concentrated tetraoxophosphate (V) acid, H_3PO_4 and kept back into the oven at a temperature of 110 °C for 24 hours. It was afterward washed repeatedly with distilled water until the pH becomes neutral. The precipitate was dried in a hot air oven at 110 °C, sieved in a 20 - 40 µm mesh size to obtain carbon particles of uniform mesh size and activated for three hours; after which it was stored in tightly closed bottle [7].

2.4 Characterization Techniques

2.4.1 Scanning electron microscopy (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The SEM has been a major technique used by various researchers [31,56,57] and it was used in this study to investigate the influence of acid activation on the activated carbon adsorbents.

2.4.2 Adsorption

Sorption involves two mechanisms: absorption and adsorption. Absorption is the uptake of a substance into the bulk sorbent via the pore structure by diffusion, whereas adsorption is a surface phenomenon by either physical forces or chemical bonding. The two processes (absorption and adsorption) occur concurrently and together are referred to as sorption. Sorbents used on water are oleophilic in nature i.e. it attracts large amount of oil without sinking. The sorbent should be easy to handle, non-toxic to the environment and biodegradable. Organic sorbents (i.e. agricultural wastes) were widely used because they are easily available and relatively inexpensive. Their sorption capacity is often as good as other inorganic sorbents because they can pick up from 5 to 15 times their weight of oil. Some of these products must be treated so that they become oleophilic [58,59].

Sorption methods involve the use of adsorbents which are porous solids with developed specific surface area, capable of binding molecules (from the liquid or gaseous phase) on its surface. Thus, these materials have a wide range of applications, especially in various types of purification technologies. Adsorbents are used for petroleum derivatives removal from coastal areas, waters, paved roads, exhaust gases and vapors. Generally, sorption methods are considered as most effective, inexpensive, available, resistant for atmospheric conditions, easy and safe; in chemical rescue, adsorbents are commonly used to immobilize and remove spills of hazardous liquids from water or paved surfaces [8,9].

They are also used in situations where it is necessary to remove residual contaminants remaining in the environment after mechanical oil collection, as well as a barrier to prevent the further spread of dangerous liquids (a protective embankment). In most cases, they can be recycled or adsorbed substance can be recovered from them [60].

The appropriate adsorbent should be chosen depending on the location of the accident and the type and quantity of spilled petroleum substance. In the selection of adsorbent, the following criteria should be taken into account: the sorption capacity of the adsorbent, its ability to immobilize oil, its buoyancy, efficiency, availability and biodegradability, possibility of recycling and/or reuse, environmental impact, price, non-flammability and resistance to chemicals and environmental conditions [61].

Recently, adsorption technology has become one of the alternative treatments in either laboratory or industrial scale. Activated carbons are known as very effective adsorbents due to their highly developed porosity, large surface area, variable characteristics of surface chemistry, and high degree of surface reactivity [6].

2.4.3 Adsorbent characterization

The morphological characteristics of the three agro-wastes (groundnut shell, banana peel and rice husk) and their activated carbon form were observed by using a scanning electron microscope (Hitachi S4800 with acceleration voltage of 15.0 kV and spot size (SE) of 200 µm) from African University of Science and Technology, Galadimawa, Abuja.

2.4.4 Batch adsorption equilibrium studies

Exactly 125 ml of the simulated oil spill of initial concentration of 0.02 g/L (Co) was used for each study. The equilibrium concentration of crude oil in water for each measured sample was determined using Perkin Elmer Lambda25 UV-VIS spectrophotometer [5]. The weight (g) of the adsorbents, volume (V) of simulated oil spill and the corresponding equilibrium concentration (C_e) were recorded. For each batch run, the quantity of crude oil adsorbed per unit weight of adsorbent denoted as q_e [5,47,62,63,64] was determined from the expression:

$$q_e = \frac{V(C_o - C_e)}{m} \tag{9}$$

According to the authors [5,47,65,66,67], the percent removal is given as:

$$\% \text{Re}\,moval = \frac{100(C_o - C_e)}{C_o} \tag{10}$$

The mean values were calculated and utilized after double runs for reproducibility errors.

2.4.4.1 Effect of adsorbent dose

About 0.02 g/L initial concentration oil sample was added to mixtures of 1.0 mg, 2.0 mg, 3.0 mg, 4.0 mg and 5.0 mg of 80 µm agro-wastes (rice husk, banana peel and groundnut shell) respectively in a 50 ml plastic bottle. The plastic bottles were placed on an orbital stirrer, and then stirred at 200 rpm at temperature of 32 ± 2 ºC for an hour each. The absorbance values were recorded carefully during the experiments; this was also repeated for the activated carbon samples of the agro-wastes.

2.4.4.2 Effect of contact time

About 0.025 g/L initial concentration oil sample was added to a mixture of 2.0 mg of 80 µm agro-wastes in a 50 ml plastic bottle. The plastic bottles were placed on an orbital stirrer, and then stirred at 200 rpm for various contact time: 15, 30, 45, 60, and 75 min. After stirring, the samples were withdrawn at the specified time intervals, filtered through a filter paper and the filtrate measured using UV-VIS spectrophotometer. The absorbance values were then recorded; this was also repeated for the activated carbon agro – waste samples.

2.4.4.3 Effect of pH

The effect of pH on crude oil adsorption was studied by agitating 2 mg of the activated carbon agro -waste in a 50 ml plastic bottle of the prepared samples with concentration of 0.025 g/L at different pH (3-11) values. The samples were agitated for 60min to reach equilibrium and agitation speed was maintained at 200 rpm. The pH of the solution was adjusted to the desired value by drop wise addition of 0.1M hydrochloric acid (HCl) and 0.1M sodium hydroxide (NaOH). After removing the adsorbent, the oil and water were filtered through a filter paper and the filtrate measured using UV-VIS spectrophotometer. The absorbance values were recorded. This was also repeated for ordinary agro-waste samples.

2.4.4.4 Effect of adsorbate dose

Batch adsorption experiments was carried out at different adsorbate dose in which 2.0 mg of the agro-wastes was shaken with 2, 4, 6, 8, and 10 g crude oil samples per 200 ml water mix in a 50 ml plastic bottle to give varying oil concentrations at 200 rpm for 60 min using constant ambient temperature, while the oil and water were filtered through a filter paper and the filtrate measured using UV-VIS spectrophotometer. The absorbance values were then taken. This was repeated for the activated carbon samples.

2.4.4.5 Effect of rotational speed

Batch experiment was carried out by adding 0.02 g/L initial concentration oil sample to a 2.0 mg 80 µm agro-wastes adsorbent in a 50 ml plastic bottle. The plastic bottles were placed on an orbital stirrer, and then stirred at constant room temperature for a specified revolution per min for 60 min. various rotational speeds of 100, 150, 200, 250 and 300 rpm were used. After stirring, the samples were withdrawn at the specified time intervals, filtered through a filter paper and the filtrate were measured using UV-VIS spectrophotometer. The absorbance values were recorded. The procedure was repeated for the activated carbon samples.

3. RESULTS AND DISCUSSION

3.1 Effect of Adsorbate Dosage on the Rate of Adsorption

The effects of adsorbate dosage were studied at temperature of 32 ± 2 °C for 2 hours using 0.02 g of each of the adsorbents. The values of quantity adsorbed at different concentrations are given in Fig. 2 and Table 1. As shown in Fig. 2, the crude oil adsorption capacity of the raw adsorbents and their activated carbon form increases with increase in adsorbate concentration. Basically this can be explained in terms of available active sites. At low adsorbate concentration, the ratio of surface active sites to crude oil was high. Hence the crude oil interacted with the sorbent to occupy the active sites on the carbon surface sufficiently, and was removed from the solution as observed in adsorption processes Table 1; with the increase in adsorbate concentration, the number of active adsorption sites on the raw adsorbents was not enough to accommodate crude oil molecules unlike the activated carbon of the adsorbents. The adsorption capacity of activated carbon of the absorbents were higher than that of the raw absorbents Table 1. The results Fig. 2 and Table 1 obtained showed that out of the agro-waste material studied activated carbon rice husk has the highest adsorption capacity at higher adsorbate concentration, hence can be used as an effective adsorbent for oil spill removal and cleanup from aqueous solution.

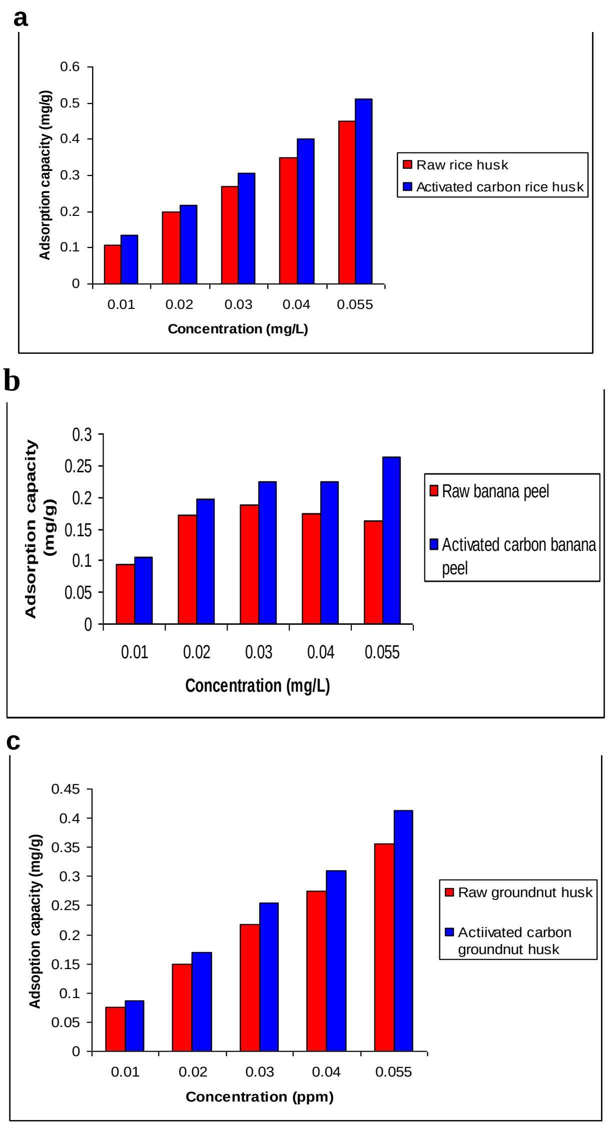


Fig. 2. Effect of adsorbate ([a]rice; [b]banana; [c]groundnut) dosage on the rate of adsorption

Table 1. Effect of adsorbate concentration on rate of adsorption of different adsorbent

S/N	W(g)	C_o (mg/l)	C_e(mg/l)	C_o-C_e(mg/l)	q_e(mg/g)	% Removal	C_e(mg/l)	C_o-C_e(mg/l)	q_e(mg/g)	% Removal
			Rice Husk				**Activated Carbon Rice Husk**			
1	0.02	0.010	0.0015	0.0085	0.1063	85.0	0.0010	0.0090	0.1125	90.0
2	0.02	0.020	0.0040	0.0160	0.2000	80.0	0.0027	0.0173	0.2163	87.0
3	0.02	0.030	0.0085	0.0215	0.2688	72.0	0.0054	0.0246	0.3075	82.0
4	0.02	0.040	0.0120	0.0280	0.3500	70.0	0.0080	0.0320	0.4000	80.0
5	0.02	0.055	0.0190	0.0360	0.4500	65.0	0.0140	0.0410	0.5125	75.0
			Banana Peel				**Activated Carbon Banana Peel**			
1	0.02	0.010	0.0025	0.0075	0.0938	75.0	0.0015	0.0085	0.1063	85.0
2	0.02	0.020	0.0062	0.0138	0.1725	69.0	0.0042	0.0158	0.1975	79.0
3	0.02	0.030	0.0150	0.0150	0.1875	50.0	0.0120	0.0180	0.2250	60.0
4	0.02	0.040	0.0260	0.0140	0.1750	35.0	0.0220	0.0180	0.2250	45.0
5	0.02	0.055	0.0420	0.0130	0.1625	23.6	0.0340	0.0210	0.2625	38.2
			Groundnut Husk				**Activated Carbon Groundnut Husk**			
1	0.02	0.010	0.0040	0.0060	0.0750	60.0	0.0030	0.0070	0.0875	70.0
2	0.02	0.020	0.0080	0.0120	0.1500	60.0	0.0064	0.0136	0.1700	68.0
3	0.02	0.030	0.0126	0.0174	0.2175	58.0	0.0096	0.0204	0.2550	68.0
4	0.02	0.040	0.0180	0.0220	0.2750	55.0	0.0152	0.0248	0.3100	62.0
5	0.02	0.055	0.0265	0.0285	0.3563	51.8	0.0220	0.0330	0.4125	60.0

3.2 Effect of contact time on the rate of Adsorption

The effect of contact time was studied at 32 ± 2 °C with 0.02 g of adsorbent. The values of adsorption capacity at different time intervals are given in Figure 3 and Table 2, the extent of crude oil removal by the raw and activated carbon adsorbents increases with increasing contact time from 15 to 60 min. Between 60-75 mins, the adsorption capacity decreased because the active sites have been filled up. The sorption and retention capacities of activated carbon adsorbents are higher than that of the raw adsorbents, this also showed that more active site was available in the activated carbon than the raw adsorbents. Results obtained as shown in Table 2 also revealed that out of the agro-wastes material studied, raw and activated carbon rice husk has higher sorption and retention capacities, hence can effectively be used for oil spill removal and cleanup from aqueous solution.

3.3 Effect of pH on the Rate of Adsorption

The effect of pH was studied using water with different pH range with 0.02g of adsorbent. The batch experiment result as shown in Fig. 3 revealed that varying the pH using the presence of either OH^- or H^+ ions compete with molecules of crude oil for adsorption site; hence the adsorbent materials and their activated carbon have high adsorption capacity at the neutral pH and acidic pH. Adsorption for both raw rice and banana husks was found to be decreasing at alkaline pH this was due to the elimination of the H^+ ions thereby promoting the activities of electrostatic repulsion between the OH^- of adsorbate and adsorbents surfaces. The activated carbon forms of the adsorbents are more favourable for oil spillage clean up in aqueous water.

3.4 Effect of Rotational Speed on the Rate of Adsorption

The effect of rotational speed was studied with 0.02g of adsorbents. The values of quantity adsorbed at different rotational speed are given in Fig. 5; the batch experiment result revealed that the adsorption of crude oil onto the adsorbents increased with rotational speed. The increase in stirring speed brought about a reduction in surface film resistance, which made the oil to get to the particle surface more easily. Surface film resistance hinders rate of adsorption. The result showed that the rate of adsorption with oil removal gradually increased with rotational speed and the most remarkable adsorption occurred at about 300 rpm for both raw and activated carbon adsorbents (Fig 5). This result also confirmed that raw and activated carbon rice husk has the highest adsorption capacity at greater rotational speed (300 rpm) as a result effective for oil spill removal from aqueous water.

3.5 Adherence to Adsorption Isotherms

Langmuir, Freundlich, Temkin and Dubinin-Radushkevich sorption isotherm models were used to examine the relationship between adsorption capacity (q_e) and aqueous concentrations (C_e) at equilibrium. Coefficient of Determination (R^2) values Table 3 of the various isotherm models for the adsorption of Crude oil on the raw and activated carbon adsorbents showed that: Langmuir isotherm was found to well represent the measured sorption data for the raw and activated banana peel while the remaining raw and activated adsorbents can be accounted for using the Temkin isotherm. This confirmed the relative importance of temperature in the energy involved for the sorption processes.

3.6 Adsorption Kinetic Models

In this study, the pseudo-first order and pseudo-second order models (equations 2 and 3) were adopted to analyse the kinetics of the adsorption process by the raw and activated carbon adsorbents. For the purpose of comparison, three types of statistical errors are employed; the applied errors are: Coefficient of determination (R^2), Average absolute relative error (AARE) and Root mean square error (RMSE). Quantitative comparison between adsorbents of the isotherms constants under various operating parameters are given in Table 4. It is observed that the pseudo-first order favoured the raw and activated carbon of rice husks and groundnut husks adsorbents better than the pseudo-second order, hence suggesting that physisorption adhesion was responsible for the adsorption of Crude oil onto these adsorbents. While the pseudo-second order favoured the raw banana peels and its activated carbon adsorbents better than the pseudo-first order, hence suggesting that chemisorption adhesion might be responsible for the adsorption of Crude oil onto this adsorbent.

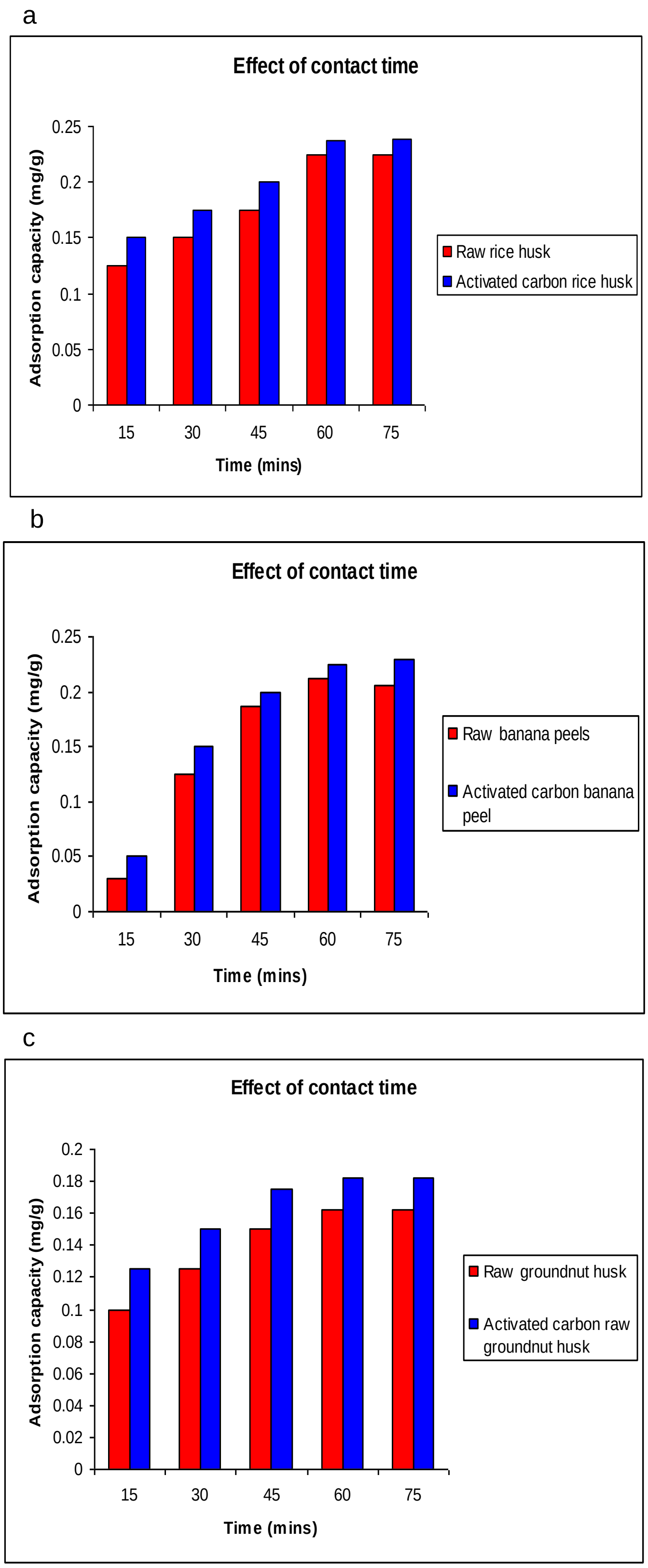
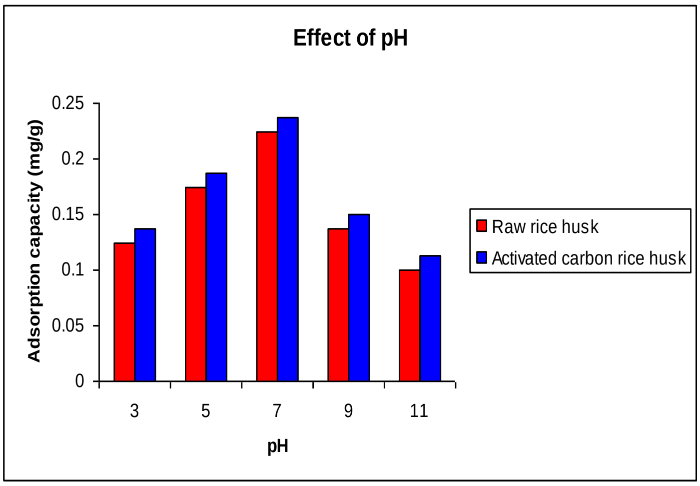


Fig. 3. Effect of contact time on the adsorption of Crude oil by different adsorbents ([a]rice; [b]banana; [c]groundnut)

Table 2. Effect of contact time on the rate of adsorption of different adsorbents

S/N	Time(min)	C_o (mg/l)	C_e(mg/l)	C_o-C_e(mg/l)	q_e(mg/g)	% Removal	C_e(mg/l)	C_o-C_e(mg/l)	q_e(mg/g)	% Removal
			Rice Husk				**Activated Carbon Rice Husk**			
1	15	0.020	0.0100	0.0100	0.1250	50.0	0.0080	0.0120	0.1500	60.0
2	30	0.020	0.0080	0.0120	0.1500	60.0	0.0060	0.0140	0.1750	70.0
3	45	0.020	0.0060	0.0140	0.1750	70.0	0.0040	0.0160	0.2000	80.0
4	60	0.020	0.0020	0.0180	0.2250	90.0	0.0010	0.0190	0.2375	95.0
5	75	0.020	0.0030	0.0170	0.2250	85.0	0.0020	0.0180	0.2250	90.0
			Banana Peel				**Activated Carbon Banana Peel**			
1	15	0.020	0.0160	0.0040	0.0500	20.0	0.0140	0.0040	0.0500	30.0
2	30	0.020	0.0100	0.0100	0.1250	50.0	0.0080	0.01200	0.1500	60.0
3	45	0.020	0.0050	0.0150	0.1875	75.0	0.0040	0.0160	0.2000	80.0
4	60	0.020	0.0030	0.0170	0.2125	85.0	0.0020	0.0180	0.2250	90.0
5	75	0.020	0.0035	0.0165	0.2063	82.5	0.0025	0.0175	0.2188	87.5
			Groundnut Husk				**Activated Carbon Groundnut Husk**			
1	15	0.020	0.0120	0.0080	0.1000	40.0	0.0100	0.0100	0.1250	50.0
2	30	0.020	0.0100	0.0100	0.1250	50.0	0.0080	0.0120	0.1500	60.0
3	45	0.020	0.0080	0.0120	0.1500	60.0	0.0060	0.0140	0.1750	70.0
4	60	0.020	0.0070	0.0130	0.1625	65.0	0.0054	0.0146	0.1825	73.0
5	75	0.020	0.0070	0.0130	0.1625	65.0	0.0054	0.0146	0.1825	73.0

a



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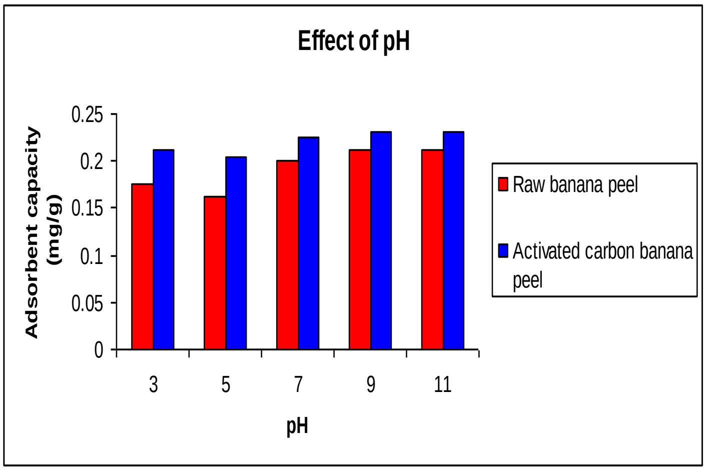

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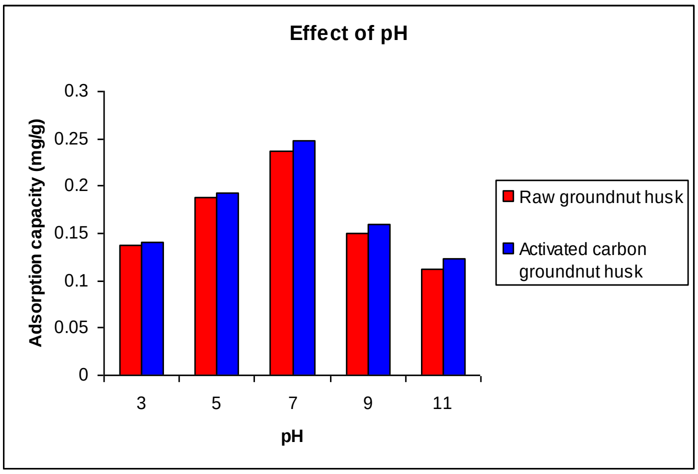

Fig. 4. Effect of pH on adsorption of crude oil over raw and activated carbon adsorbents ([a]rice; [b]banana; [c]groundnut)

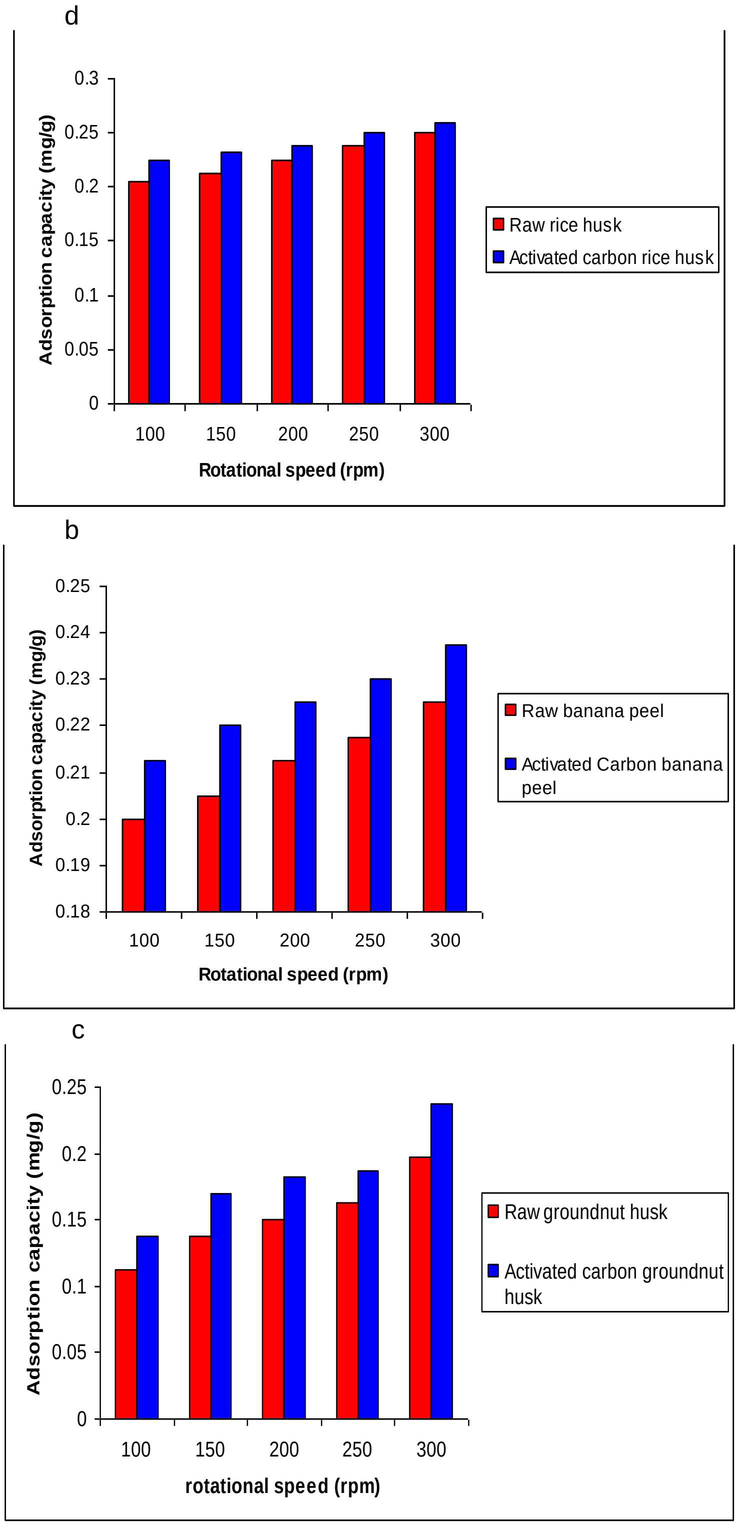

Fig. 5. Effect of Rotational Speed on Adsorption of oil on Raw and Activated Carbon Adsorbents ([a]rice; [b]banana; [c]groundnut)

3.7 Characteristic of the Adsorbents

Scanning electron microscopy (SEM) technique was employed to observe the surface physical morphology of the samples used as absorbents in this study (Figs 6-8).

The SEM images of the raw rice and raw groundnut husks before adsorption and after adsorption showed a similar significant difference of the surface topography between them was observed (Figs 6-7). The image of the raw rice husks and raw groundnut husks before adsorption of crude oil showed a porous less regular surface, whereas remarkably regular and homogenous surface morphology are observed for the two husks after adsorption.

It was also observed from the micrographs that the surface of the activated carbon rice husk and activated carbon groundnut before adsorption was full of cavities. A gradual improvement was observed on the surface morphology with the chemical activation; the SEM images of the activated carbon of both husks after adsorption of crude oil showed larger area of clusters than on the sample before adsorption.

Table 3. Coefficient of determination (R^2) of sorption isotherm models

Adsorbents	Langmuir	Freundlich	Temkin	Dubinin-Radushkevich
	Coefficient of Determination (R^2)			
Rice Husk	0.9613	0.8140	0.9933	0.7560
Activated Carbon Rice Husk	0.9921	0.8210	0.9956	0.8134
Banana Peel	0.9409	0.8828	0.8447	0.6946
Activated Carbon Banana Peel	0.9638	0.8871	0.8547	0.8428
Groundnut Husk	0.9350	0.8141	0.9907	0.9901
Activated Carbon Groundnut Husk	0.9629	0.8210	0.9861	0.9856

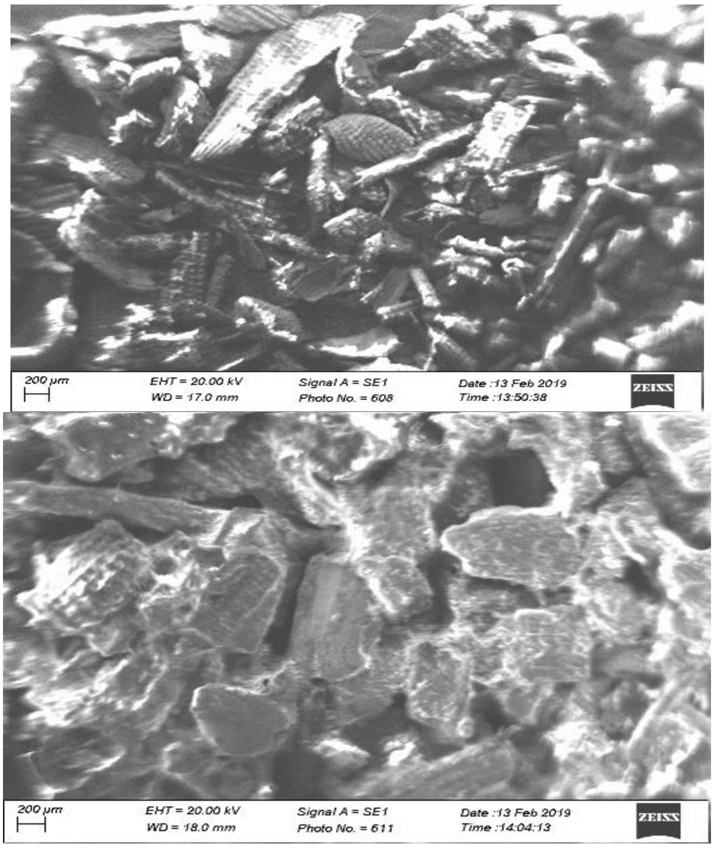

Fig. 6a. SEM image of raw rice husk before and after adsorption

Table 4. Calculated errors of adsorption kinetic models

	Pseudo First Order						Pseudo Second Order				
Adsorbents	**q_e Expt (mg/g)**	**k_1 min^{-1}**	**q_e Calc. (mg/g)**	**R^2**	**AARE**	**RMSE**	**k_2 min^{-1}**	**q_e Calc. (mg/g)**	**R^2**	**AARE**	**RMSE**
Rice Husk	0.540	-0.045	0.200	0.965	0.126	0.152	0.001	-6.540	0.953	2.622	3.166
Activated Carbon Rice Husk	1.559	-0.030	0.573	0.980	0.126	0.441	0.002	5.810	0.960	0.545	1.901
Banana Peel	0.540	0.013	0.004	0.896	0.199	0.240	0.015	-0.408	0.971	0.351	0.424
Activated Carbon Banana Peel	1.559	0.019	0.015	0.878	0.198	0.690	0.015	-0.416	0.994	0.253	0.883
Groundnut Husk	0.540	-0.045	0.200	0.995	0.126	0.152	0.001	-6.540	0.958	2.622	3.166
Activated Carbon Groundnut Husk	1.559	-0.030	0.573	0.997	0.126	0.441	0.002	5.810	0.965	0.545	1.901

The SEM technique employed to observe the surface physical morphology of the raw banana peels before and after adsorption is as shown in Fig 8. A significant difference of the surface topography between the two surfaces (i.e. the raw and activated carbon) was

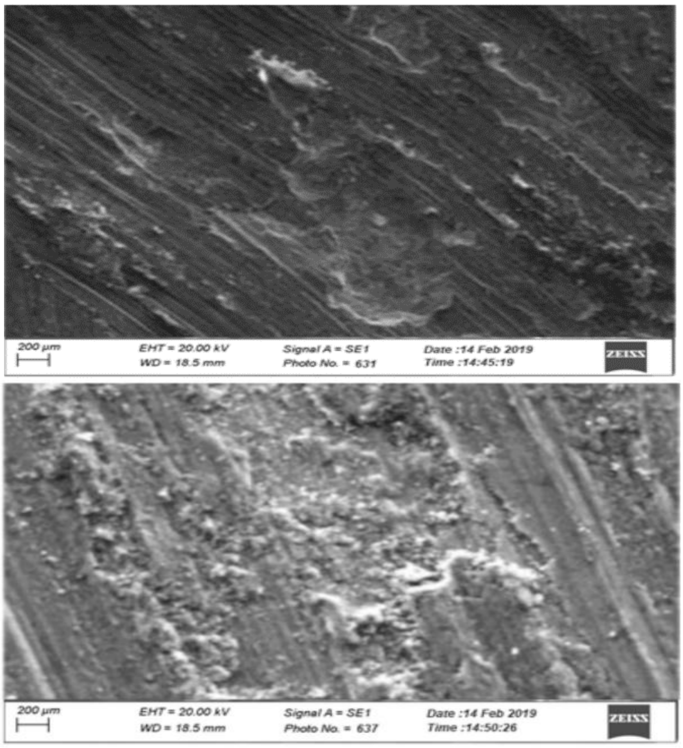

Fig. 6b. SEM image of raw groundnut husk before and after adsorption

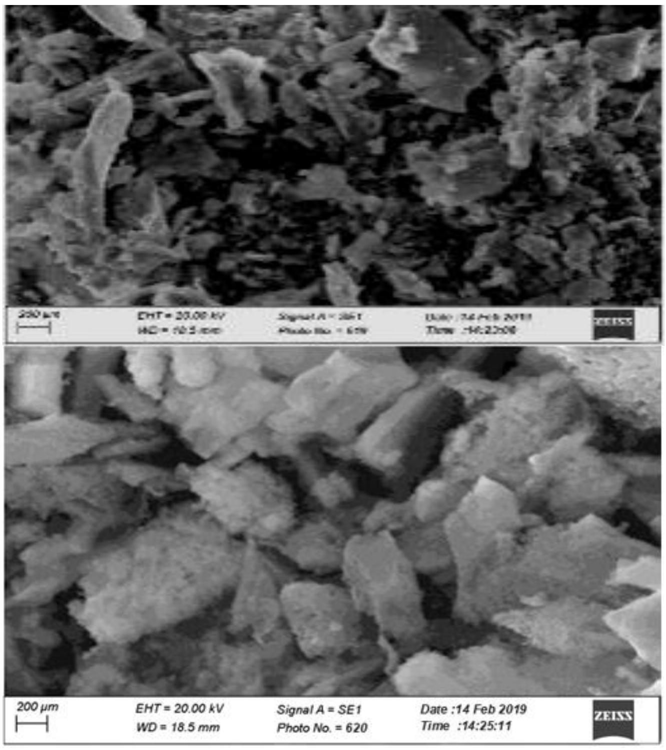

Fig. 7a. SEM image of activated carbon rice husk before and after adsorption

observed, the image of the raw banana peels before adsorption showed a smooth surface with slit like cracks and voids, relatively organized on the surface, while in another region both raw adsorbents revealed porous less regular surface; whereas remarkably regular and homogenous surface morphology were detected for the raw banana peels after adsorption.

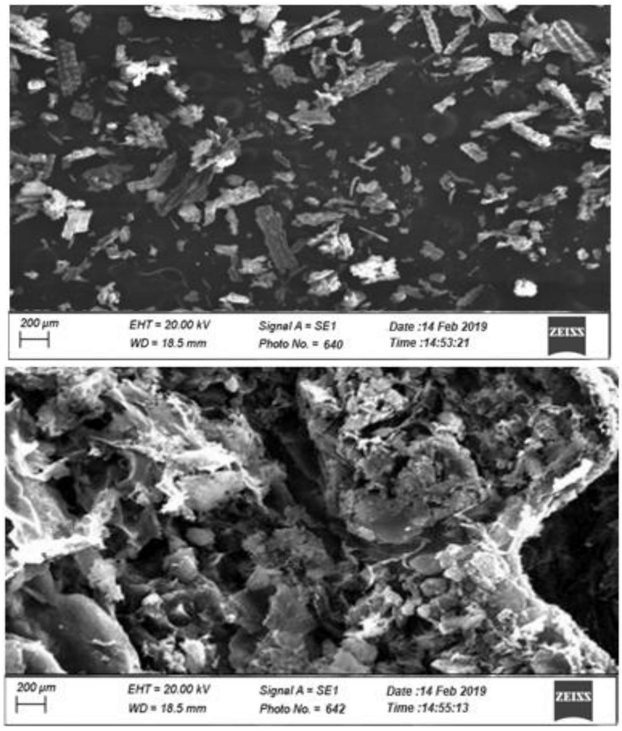

Fig. 7b. SEM image of activated carbon groundnut husk before and after adsorption

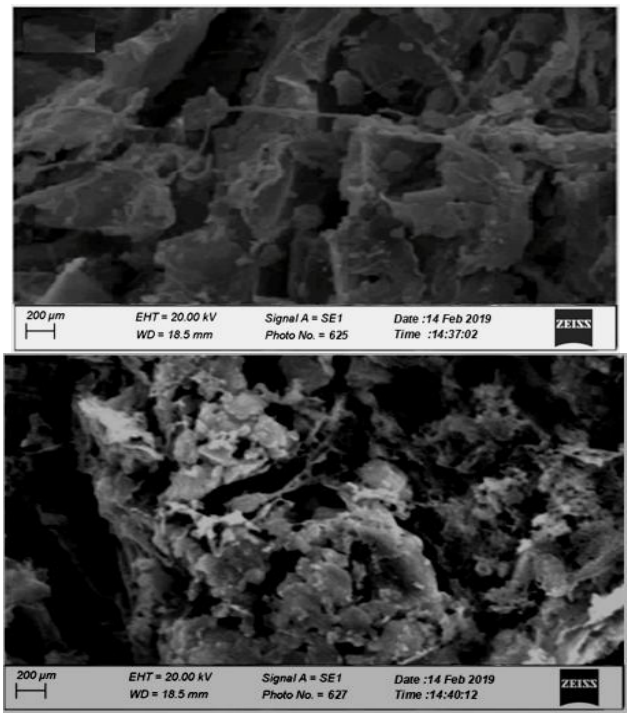

Fig. 8a. SEM image of raw banana peel before and after adsorption

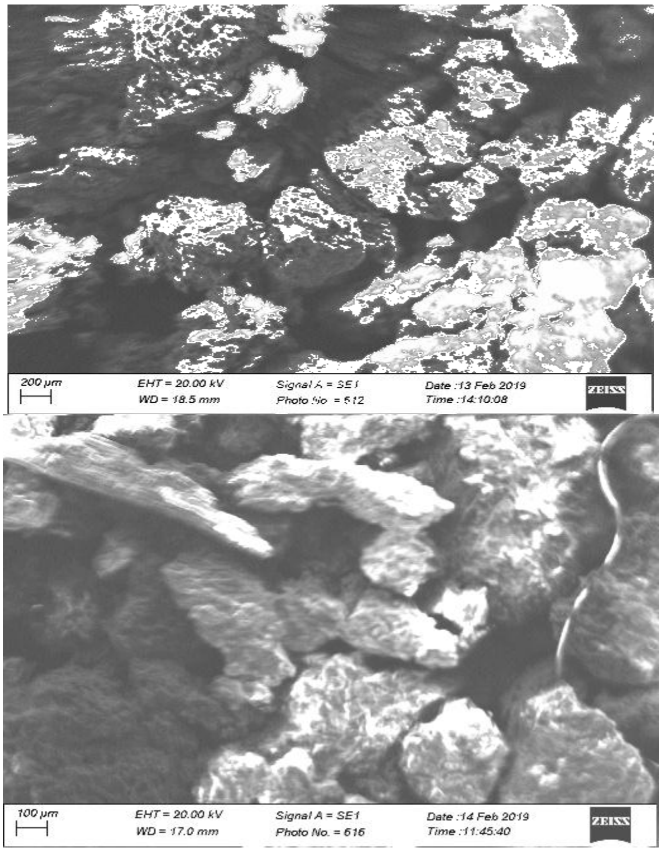

Fig. 8b. SEM image of activated carbon banana peel before and after adsorption

It was observed from the micrographs that the external surface of the activated carbon of both adsorbents before adsorption was full of cavities. A gradual improvement was detected on the surface morphology with the chemical activation, the surface of the activated carbon before adsorption is smoother and more porous structured than that of the raw adsorbents. As seen in the images, crater like macropores formed during the reactions between the raw adsorbents and H_3PO_4. Examination of the image clearly reflects that the holes on the particles are in macropore size and have various geometry.

Adsorbent hydrophobization was carried out by activating each of the agricultural waste thus, increasing their ability to absorb crude oil.

4. CONCLUSION

This study examined oil adsorption processes using raw agricultural wastes (rice husk, banana peels and groundnut shells) and their activated carbon form. The following indicators were used to compare sorption efficiency of the test objects: adsorbate dosage, contact time, pH, rotational speed, adsorption isotherms, adsorption kinetic models and SEM techniques.

The results of the experiment demonstrated that the activated carbon form of all the agro-wastes used has high and better adsorption capacity making them competitive with the raw agricultural wastes. This can be attributed to the fact that hydrophobic materials are considered to be the most efficient adsorbents for organic compounds from water solutions, as their adsorption is mainly based on the dispersion force. Dispersion interaction of the organic molecules with carbonic structures of the hydrophobic adsorbent surface is much stronger than interaction of carbonic sorbents with the water molecules. Results from this study revealed that activated carbon adsorbents may be used as cost-effective adsorbents to clean-up oil spills from polluted water.

For all the agro-waste absorbents used result revealed that neutral pH was more effective and favourable in crude oil uptake. It was also observed from the adsorption kinetic models used in this study that adsorption of crude oil the raw and activated carbon of rice and groundnut husks adsorbents was better described by the pseudo-first order signifying that physisorption adhesion was responsible for the adsorption; while the pseudo-second order defined the raw banana peels and its activated carbon adsorbents telling that chemisorption adhesion was accountable for the adsorption of Crude oil onto this adsorbent.

In conclusion, this study revealed the possibility to obtain effective crude oil adsorbents from raw and activated carbon form of rice husk, banana peels and groundnut shells, which are considered as agricultural waste; and also offers worthy waste management approach.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sdiarticle4.com/review-history/66589